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4. TITLE AND SUBTITLE Final Report: Spatial Distribution of Amorphization Intensity in B4C during Rate-Dependent Indentation and Ballistic Impact Processes [1.2 Solid Mechanics]			5a. CONTRACT NUMBER W911NF-14-1-0230		
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6. AUTHORS Ghatu Subhash			5d. PROJECT NUMBER		
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT At high pressures, such as those encountered in ballistic impact, boron carbide (B4C) suffers from loss of crystallinity, referred to as 'amorphization', to form nanometer scale amorphous bands. Through experimental and theoretical investigations, current research seeks to enhance our understanding of B4C crystal structure (polymorphism) so as to explore novel avenues for improving its resistance to amorphization. The objectives of this research are to (a) measure the size and shape of the amorphized zones beneath static and dynamic indentations, (b) determine residual stress distribution in the vicinity of the amorphized regions, (c) develop a dynamic expanding					
15. SUBJECT TERMS Boron Carbide, Indentation, Amorphization, Raman spectroscopy, Expanding Cavity Model, Polymorphs					
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a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 352-392-7005

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Final Report for Period Beginning 10-Jun-2014 and Ending 09-Jun-2017

Title: Spatial Distribution of Amorphization Intensity in B4C during Rate-Dependent Indentation and Ballistic Impact Processes [1.2 Solid Mechanics]

Begin Performance Period: 10-Jun-2014

End Performance Period: 30-Oct-2017

Report Term: 0-Other

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STEM Degrees: 5

STEM Participants: 9

Major Goals: The goal is to investigate the relationship between the indentation-induced amorphization zone size and the impact-induced amorphization zone size and draw parallels to the rate-dependent mechanics of the amorphization process. Due to the small volume of the amorphization zone, the indentation models are useful for calibrating the continuum or multiscale models of the amorphization process and develop fundamental understanding of their growth process. Then these models can be extended to ballistic impact processes. With the above goal in mind, the following objectives are identified in this research:

1. Determination of the rate-dependent evolution of amorphization zone size and its intensity distribution during indentation and high velocity impact loads.
2. Compare and contrast the differences in the intensity and size of the amorphized zone using Raman spectroscopy and identify the differences in deformation and damage mechanisms as a function of indenter load (pressure) and indenter velocity.
3. Develop mechanistic models for initiation and growth of amorphization process based on the observed features on the size and intensity of the amorphization zone beneath the surface as a function of imposed pressure and strain rate (velocity).

To accomplish the above objectives a range of experiments consisting of static and dynamic indentations as well as high velocity projectile impacts will be conducted on armor grade B4C ceramic. The subsurface regions will be evaluated using Raman spectroscopy, optical microscopy and scanning electron microscopy.

Accomplishments: The results of the investigation reveal that (i) amorphization induces volume change and causes compressive residual stress in the surrounding crystalline matrix, (ii) computational Raman spectroscopy can be effectively used to decipher the constituent polymorphs in a fabricated B4C, (iii) cage spaces that exist in the B4C crystal lattice are responsible for its low density and propensity for amorphization, and (iv) these spaces can be used to dope B4C to make it amorphization resistant.

More specific details are provided below:

1. A procedure was developed to (i) determining the depth of material removed in each polishing stage beneath an indented surface and (ii) quantify the amorphization intensity utilizing D-peak area (which corresponds to amorphization) from the Raman spectrum on boron carbide. From the analysis of data, 3D maps of amorphization zones were generated for four static and three dynamic indentation loads. The results are shown in Fig. 1, and the details are published in "Raman Spectroscopy Mapping of Amorphized Zones Beneath Static and Dynamic Vickers Indentations on Boron Carbide," G. Parsard and G. Subhash, Journal of the European Ceramic Society 37 (2017) 1945-1953.

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2. Similar indentation experiments and Raman spectroscopic analysis of large grain (10 microns) and ultrafine grained B₄C (0.3 microns) revealed that severity of amorphization is reduced when the grain size is decreased, as shown in Fig. 2. In addition, the ultrafine-grained material showed improvements in static hardness and compressive strength across all strain rate regimes, and also exhibited improved fracture toughness in comparison to the larger-grained material. These results are published in M. DeVries et al., "Rate-Dependent Mechanical Behavior and Amorphization of Ultrafine-Grained Boron Carbide," *Journal of the American Ceramic Society*, (2016) 3398-3405.

3. TEM analysis of deformed B₄C regions revealed that amorphized regions contain dislocations and amorphization causes lattice distortion leading to residual stresses and initiation of micro cracks. These results are published in an Editor Invited Viewpoint Article, "In Search of Amorphization-Resistant Boron Carbide" G. Subhash, A.P. Awasthi, C. Kunka, P. Jannotti and M. DeVries, *Scripta Materialia* (2016) 158-162.

4. 3D maps of residual stress were generated for static and dynamic Vickers indentations based on the concurrent shift of the 1088 cm⁻¹ peak in the Raman spectra. Residual stress appears to be higher near the intact amorphized regions and lower near cracks due to stress relaxation and graphitic inclusions which buffer the stress. The results also suggest that the process of amorphization causes a volumetric expansion of the affected material relative to its formerly pristine crystalline state. This expansion causes compressive residual stress in the surrounding crystalline matrix which may be responsible for the observed amorphous peak in the Raman Spectrum. In addition, dislocations and lattice rotation surrounding the amorphized islands were also argued to impart residual stresses in the material. The manuscript containing these results, titled "Amorphization-Induced volume change and residual stresses in Boron Carbide", has been submitted to *Journal of the American Ceramic Society* and is awaiting peer review.

5. Using density functional theory (DFT) the theoretical Raman spectra for more than 50 polymorphs were evaluated and a procedure for identifying the polymorphs formed in a fabricated boron carbide sample was developed. The procedure has been shown to be applicable on hot pressed (HP) and spark plasma sintered (SPS) boron carbide specimens. These results are published in two papers: (i) C. Kunka, A. Awasthi, G. Subhash, "Evaluating boron-carbide constituents with simulated Raman spectra" *Scripta Materialia*, 138 (2017) 32-34; and (ii) C. Kunka, A.P. Awasthi, and G. Subhash, "Crystallographic and spectral equivalence of boron-carbide polymorphs," *Scripta Materialia*, 122 (2016) 82-85.

6. The DFT study also identified large cage spaces in the boron carbide crystal structure which have been postulated to be responsible for its low density as well as its propensity for amorphization. The cage space is large enough to accommodate large atoms which can potentially mitigate the propensity for amorphization by providing bending resistance for the chain atoms of the unit cell. Based on the size of the cage space and atomic radii of elements, a large number of atoms are identified as potential dopants for boron carbide. These results are published in an Editor Invited Viewpoint Article: "In Search of Amorphization-Resistant Boron Carbide" G. Subhash et al., *Scripta Materialia* (2016) 158-162.

7. Based on the literature review it was identified that when boron carbide disassociates during amorphization, new constituents such as (B₁₂)CCC, B₁₂ and graphite are formed. However, their Raman peaks did not coincide with the amorphous peak measured. Further DFT-simulations were performed to seek the dependence of the α -boron (α -B₁₂), (B₁₂)CCC and graphite constituents on the Raman spectra at different levels of hydrostatic pressure ranging from 0-150 GPa. It was found that these constituents must be stressed in the range of 60-110 GPa to occupy the amorphous spectral locations. This suggests that the region around the amorphous zone must be locked in a high stress state even after unloading, leading to a new understanding of the immediate region surrounding the amorphous zone. The combined spectrum is a superposition of spectra emanating from all regions. This work is being submitted to *Progress in Materials Science*.

8. An extended Mohr-Coulomb model was developed to capture the normalized pressure-dependent shear strength of a variety of brittle materials over a wide range of pressures. This model is not only able to capture the linear response of brittle ceramics at low pressures, but also the experimentally observed nonlinear response at higher pressures up to HEL and the pressure-independent response beyond HEL with a single curve. Further, the constants used in this model are shown to be universal and applicable to most brittle materials. Utilizing the extended Mohr-Coulomb model, an improved dynamic expanding cavity model (d-ECM) was developed, which more accurately captures the experimentally observed target resistance of structural ceramics. This model is less computationally demanding than the conventional dynamic expanding cavity model. The new d-ECM, allows the model to be used to estimate a material's ballistic capability without the need for additional experimental data. A sensitivity analysis using the d-ECM revealed that the properties of the comminuted ceramic, particularly its dynamic shear strength, has a greater influence on the target resistance of ceramics than those of the corresponding intact material. These results are published in "An Improved Dynamic Expanding Cavity Model for High-Pressure and High-Strain Rate Response of Ceramics" S. Bavdekar, G. Parsard, G. Subhash, and S. Satapathy, *International Journal of Solids and Structures*, (2017) 77-88

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Training Opportunities: 6-PhD students (2 minorities), 1 post-doc and 2 undergraduate students (minorities) were partially supported and trained in ceramics, high strain rate testing, material characterization and microscopy and spectroscopy. Few also received training in computational spectroscopy.

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Results Dissemination: Peer-reviewed journal articles (including those under review)

1. C. Kunka+, A.P. Awasthi (PG), and G. Subhash*, "Evaluating Boron-Carbide Constituents with Simulated Raman Spectra" *Scripta Materialia* 138 (2017) 32-34
<http://dx.doi.org/10.1016/j.scriptamat.2017.05.030>
2. G. Parsard+ and G. Subhash*, "Raman Spectroscopy Mapping of Amorphized Zones Beneath Static and Dynamic Vickers Indentations on Boron Carbide," *Journal of the European Ceramic Society* 37 (2017) 1945-1953;
<http://dx.doi.org/10.1016/j.jeurceramsoc.2016.12.045>
3. S. Bavdekar+, G. Parsard+, G. Subhash*, and S. Satapathy "An Improved Dynamic Expanding Cavity Model for High-Pressure and High-Strain Rate Response of Ceramics" *International Journal of Solids and Structures* 125 (2017) 77-88 <https://doi.org/10.1016/j.ijsolstr.2017.07.014>
4. G. Subhash*, A.P. Awasthi (PG), C. Kunka+, P. Jannotti+ and M. DeVries+, "In Search of Amorphization-Resistant Boron Carbide" Editor Invited 'Viewpoint Article' in *Scripta Materialia* (2016) 158-162; doi:10.1016/j.scriptamat.2016.06.012
5. C. Kunka (G), A.P. Awasthi (PG), and G. Subhash*, "Boron-carbide polymorphs: nomenclature, equivalence and Raman spectra", *Scripta Materialia*, 122 (2016) 82-85
doi:10.1016/j.scriptamat.2016.05.010
6. S. Bavdekar and G. Subhash, "Comparison of Pressure-Sensitive Strength Models for Ceramics Under Ultrahigh Confinement", *Journal of the American Ceramic Society* (in review, Sep 2017)
7. G. Parsard and G. Subhash, "Amorphization-Induced volume change and residual stresses in Boron Carbide" *Journal of the American Ceramic Society* (in review, Sep 2017)
8. A. Awasthi and G. Subhash, "Deformation behavior of boron-rich icosahedral ceramics" (manuscript being prepared for submission to *Progress in Materials Science* (Dec 2017)

Conference Presentations:

1. Plenary Speaker at the International Conference on Molecular Spectroscopy (ICMS 2017), "Deciphering the Link between Deformation Behavior and Raman Spectra for Polymorph-Level Tailoring of Boron Carbide" 8-10 December 2017, Kottayam, Kerala, India
2. Session Keynote Speaker of the Session on 'Dynamic response and failure of advanced materials -5', (topic 12-16), "Deciphering the Link between Deformation Behavior and Raman Spectra for Polymorph-Level Tailoring of Boron Carbide" Organized by Prof. Luoyu Roy Xu of University of New Mexico, at the ASME-IMECE, Tampa, FL, November 5-9, 2017
3. Session main speaker at the 2017 Mach Conference "Deciphering the link between Raman spectrum and deformation behavior of boron carbide polymorphs" Mach Conference, Johns Hopkins University, Annapolis, MD. (April 5-7, 2017)
4. Invited speaker at the International Conference on Advanced Ceramics and Composites (ICACC 2017), symposium on "Armor Ceramics", Daytona Beach, FL Jan 23-27 (2017).
5. Plenary Lecture at the 1st International Conference on Alumina and Other Functional Ceramics (AOFC-2015) "Characterization of Microstructure, Composition, Microresidual Stresses and Phase Transformations in Advanced Structural Ceramics by Raman Spectroscopy" CSIR-Central Glass and Ceramic Research Institute, Kolkata, India, Indian Ceramic Society, 11-13 March 2015.
6. Invited Speaker at the 18th International Symposium on Boron, Borides and Related Materials, "Characterization of Amorphized Zone due to High-Pressure Loading in Boron Carbide", Honolulu, Hawaii, Aug 31-Sept 2014.
7. Invited Lecture at the 5th International Conference on Perspectives in Vibrational Spectroscopy, "Raman Spectroscopy for Determination of Macro and Micro Residual Stresses and Structural Disorder in Ceramics" Thiruvananthapuram, Kerala, India, 08-12 July 2014
8. Invited Speaker at the "Dynamic Behavior of Materials VI - TMS/SMD Symposium in Honor of Professor Marc Meyers" Feb 16-20, 2014 TMS Annual Meeting & Exhibition, San Diego, CA "Influence of Stress State and Strain Rate on Amorphization in Boron Carbide"
9. "Ultrahigh pressure deformation and Raman spectra of Boron carbide" 15th Conference and Exhibition of the European Ceramic Society (ECerS), Budapest, Hungary, July 9-13, 2017.
10. "Deciphering the influence of pressure and strain rate on fracture strength of structural ceramics" ASME-IMECE2016, Phoenix, AZ, Nov 13-17, 2016
11. "Rate Dependent Amorphization Behavior of Boron Carbide", 17th International Conference on Experimental Mechanics (ICEM17), Rhodes, Greece, July 3 - 7, 2016.
12. "Which one has More Influence on Failure Strength of Ceramics: Pressure or Strain Rate?" Mach Conference, Apr 5-8, 2016, Annapolis, MD.
13. "Predicting Raman Spectra of Boron Carbide Polymorphs" Mach Conference, Apr 5-8, 2016, Annapolis, MD.

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- 14 "Transmission Electron Microscopy of Amorphization Band Structure due to Rate-Dependent Indentation on Micro- and Nano-Grained Boron Carbide" (ICACC-S4-024-2016) 40th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, Jan 25-29, 2016.
- 15 "Prediction of Raman Spectra and Shear Resistance of Boron Carbide using Density Functional Perturbation Theory" (ICACC-S4-021-2016) 40th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, Jan 25-29, 2016.
- 16 "Comparison of Amorphized Zones Beneath Static and Dynamic Indentations in Boron Carbide". (ICACC-S4-030-2016) 40th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, Jan 25-29, 2016.
- 17 "Rate-dependent Hardness and Amorphization Response of Nano-grained Boron Carbide" (ICACC-S4-P044-2016) 40th International Conference and Exposition on Advanced Ceramics and Composites in Daytona Beach, FL, Jan 25-29, 2016.
- 18 "Characterization of Biaxial Residual Stresses and Phase Transformations in Ceramics using Raman Spectroscopy" 2015 European Solid Mechanics Conference (ESMC2015), Madrid, July 6-10, 2015

Honors and Awards: Ghatu Subhash

- National Academies Panel member for 'Ballistic Science and Engineering' at the Army Research Laboratories, National Research Council 2015-2017
- '2018 Frocht Award', (to receive in June 2018) Society for Experimental Mechanics (SEM) - in recognition of outstanding achievements as an educator. The award recognizes the Experimental Mechanics Educator of the Year and is in recognition of the technical stature and the high personal regard in which the awardee is held by the experimental mechanics community.
- Fellow, Society of Experimental Mechanics (June 2014)
- "Significant Contribution Award" (June 2014), American Nuclear Society (ANS) Materials Science and Technology Division (MSTD)
- Orr 'Best Paper' Award, ASME-Journal of Engineering Materials and Technology 2016
- 'Technology Innovator Award', University of Florida 2016
- 'College of Engineering Doctoral Dissertation Advisor/Mentoring Award', University of Florida 2015-2016
- Associate Editor, Experimental Mechanics journal 2014-2016
- Associate Editor, ASME Journal of Engineering Materials and Technology 2014-present
- Associate Editor, Mechanics of Materials, an International Journal 2008-present
- Associate Editor, Journal of the American Ceramic Society 2006-present

Gregory Parsard (Ph.D., graduated)

- NSF Graduate Research Fellowship Program (NSF GRFP) 2011-2016
- 2nd place - Student Paper Competition at the Society of Experimental Mechanics, Lombard, IL (June 2013)

Cody Kunka (Graduate Student)

- NSF Graduate Research Fellowship Program (NSF GRFP) 2015-present
- '2nd place International Student Presentation Competition' at the 2014 Annual SEM conference and Exposition, June 4-7, 2014, Greenville, SC
- Finalist in Florida Statewide Graduate Student Research Symposium 2016
- Honorable Mention in the Elegance of Science Art Competition 2017
- Mechanical & Aerospace Engineering Graduate Student Research Award 2017

Matthew DeVries (Graduate student)

- NSF Graduate Research Fellowship Program (NSF GRFP) 2016-present
- DoD-NDSEG Fellowship offered (declined in order to accept NSF GRFP) 2016
- Sung and Yvonne Lu Graduate Fellowship Award 2017
- 2nd Place at the Young Stress Analyst competition conducted in conjunction with the 10th International Conference on Experimental Mechanics by the British Society for Strain Measurement (BSSM) at Edinburgh, Scotland, Sept 1-4, 2015. He received free boarding and registration by BSSM and travel cost was paid by the UF.

Alison Trachet (Graduate Student)

Received 2015-16 Fulbright U.S. Student Award to Austria (Mar 2015)

Protocol Activity Status:

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Technology Transfer: The PI has interacted extensively with researchers at ARL, Aberdeen Proving Ground. The following Collaborations and Technology Transfer have occurred

- At the invitation of Dr. J.P. Singh (ARL, former Head of Structural Ceramics Division) and Dr. Mark Tschopp (ARL), the PI presented a technical seminar at ARL on December 15, 2016, titled "Deciphering the link between Raman spectra and deformation mechanisms in boron carbide".
- The PI has shared more than 400,000 Raman spectra on boron carbide (developed as a part of previous project) with Dr. Mark Tschopp (ARL) for validation of newly developed models by his group at ARL.
- The PI has collaborated with Dr. Sikhanda Satapathy (ARL) to improve the existing dynamic expanding cavity model for brittle ceramics. A paper was co-authored in the International Journal of Solids and Structures, (2017), S. Bavdekar, G. Parsard, G. Subhash., S. Satapathy "An Improved Dynamic Expanding Cavity Model for High-Pressure and High-Strain Rate Response of Ceramics"
- Impact tests were performed on boron carbide disks using spherical projectiles at ARL by Dr. Phillip Jannotti under the supervision of Dr. Jerry LaSalvia (ARL). CT scans of the impacted specimens were performed by Dr. Timothy Walter (ARL). The subsurface damage and severity of amorphization are being assessed using Raman spectroscopy at the PI's lab.
- The PI taught a 2-day technical course on March 7-8, 2017 on "Dynamic response of ceramics and transparent materials" at Johns Hopkins University/HEMI (Hopkins Extreme Materials Institute)/MEDE (Materials in Extreme Dynamic Environments). The course was attended by approximately 25 individuals from ARL, Johns Hopkins University, and Ceradyne, Inc., Corning, Inc., etc.
- The PI served as National Research Council's National Academies Panel member for 'Ballistic Science and Engineering' at the Army Research Laboratories during June 5-7, 2017 and June 22-24, 2015 at Aberdeen Proving Ground.

PARTICIPANTS:

Participant Type: Faculty

Participant: Ghatu Subhash

Person Months Worked: 3.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Gregory Parsard

Person Months Worked:

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member:

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Salil Bavdekar

Person Months Worked: 15.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Amnaya Awasti

Person Months Worked: 15.00

Funding Support:

Project Contribution:

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International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Cody Kunka

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Mathew DeVries

Person Months Worked: 6.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Other Professional

Participant: Muhammed Shafiq

Person Months Worked: 1.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Other Professional

Participant: Alison Trachet

Person Months Worked: 2.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student

Participant: Amanda Wei

Person Months Worked: 6.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student

Participant: Salinas Santiago

Person Months Worked: 6.00

Funding Support:

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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student

Participant: Douglas Steinbach

Person Months Worked: 1.00

Funding Support:

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

DISSERTATIONS:

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Title: SPATIAL DISTRIBUTION OF AMORPHIZATION INTENSITY IN BORON CARBIDE DURING RATE-DEPENDENT INDENTATION AND IMPACT PROCESSES

Authors: Gregory Parsard

Acknowledged Federal Support: Y

Scientific Progress and Accomplishments: # W911NF-14-1-0230
(Reporting Period: 06/10/2014 – 06/09/2017)

Spatial Distribution of Amorphization Intensity in B₄C during Rate-Dependent Indentation and Ballistic Impact Processes

Ghatu Subhash

Department of Mechanical and Aerospace Engineering
University of Florida, Gainesville, FL, 32611

Abstract

At high pressures, such as those encountered in ballistic impact, boron carbide (B₄C) suffers from loss of crystallinity, referred to as ‘amorphization’, to form nanometer scale amorphous bands. Through experimental and theoretical investigations, current research seeks to enhance our understanding of B₄C crystal structure (polymorphism) so as to explore novel avenues for improving its resistance to amorphization. The objectives of this research are to (a) measure the size and shape of the amorphized zones beneath static and dynamic indentations, (b) determine residual stress distribution in the vicinity of the amorphized regions, (c) develop a dynamic expanding cavity model for ceramics to determine their ballistic resistance, and (d) to simulate the effect of various states of stress upon atomistic response and Raman spectra of B₄C polymorphs. The results of the investigation reveal that (i) amorphization induces volume change and causes compressive residual stress in the surrounding crystalline matrix, (ii) computational Raman spectroscopy can be effectively used to decipher the constituent polymorphs in a fabricated B₄C, (iii) cage spaces that exist in the B₄C crystal lattice are responsible for its low density and propensity for amorphization, and (iv) these spaces can be used to dope B₄C to make it amorphization resistant.

Approach

- Vickers indentations were made at quasistatic and dynamic strain rates on boron carbide specimens with an average grain size of 15 μm using loads ranging from 1.7 N to 13.7 N to determine the rate-dependent evolution of amorphized zone size and distribution of amorphization intensity beneath indentations. The material beneath each indentation was probed through alternating sessions of polishing and Raman spectroscopy. The resulting Raman scans were then analyzed to quantify the residual stress and intensity of amorphization in the material. Maps of the amorphization intensity and residual stress distribution surrounding each indentation were generated from the analyzed data.
- The grain size dependence (10 micron versus 0.3 micron) of mechanical properties, strain rate sensitivity, and propensity for amorphization in boron carbide were investigated using a range of mechanical tests (indentation, compressive loading, and fracture toughness) and Raman spectroscopy.
- A modified dynamic expanding cavity model (d-ECM) was developed from a recently proposed extended Mohr-Coulomb model in order to characterize the target resistance of ceramics due to ballistic impact.
- For the first time, density functional theory (DFT) and density functional perturbation theory (DFPT) calculations were performed to examine the vibrational spectra of boron carbide polymorphs under hydrostatic and shear loads.

Accomplishments for Reporting Period

1. A procedure was developed to (i) determining the depth of material removed in each polishing stage beneath an indented surface and (ii) quantify the amorphization intensity utilizing D-peak area (which corresponds to amorphization) from the Raman spectrum on boron carbide. From the analysis of data, 3D maps of amorphization zones were generated for four static and three dynamic indentation loads. The results are shown in Fig. 1, and the details are published in “Raman Spectroscopy Mapping of Amorphized Zones Beneath Static and Dynamic Vickers Indentations on Boron Carbide,” G. Parsard and G. Subhash, *Journal of the European Ceramic Society* 37 (2017) 1945-1953.

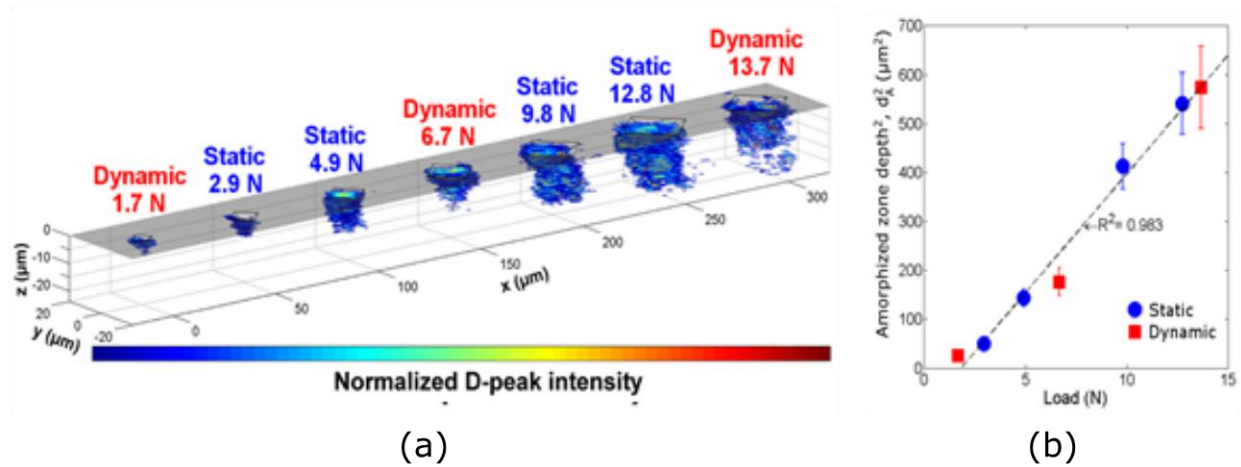


Fig. 1. (a) Amorphized zones developed beneath static and dynamic Vickers indentations and (b) plot revealing that amorphized zone depth is only a function of load but not rate of loading.

- Similar indentation experiments and Raman spectroscopic analysis of large grain (10 microns) and ultrafine grained B₄C (0.3 microns) revealed that severity of amorphization is reduced when the grain size is decreased, as shown in Fig. 2. In addition, the ultrafine-grained material showed improvements in static hardness and compressive strength across all strain rate regimes, and also exhibited improved fracture toughness in comparison to the larger-grained material. These results are published in M. DeVries, J. Pittari, G. Subhash, K. Mills, C. Haines, J. Zheng. “Rate-Dependent Mechanical Behavior and Amorphization of Ultrafine-Grained Boron Carbide,” *Journal of the American Ceramic Society*, (2016) 3398-3405.

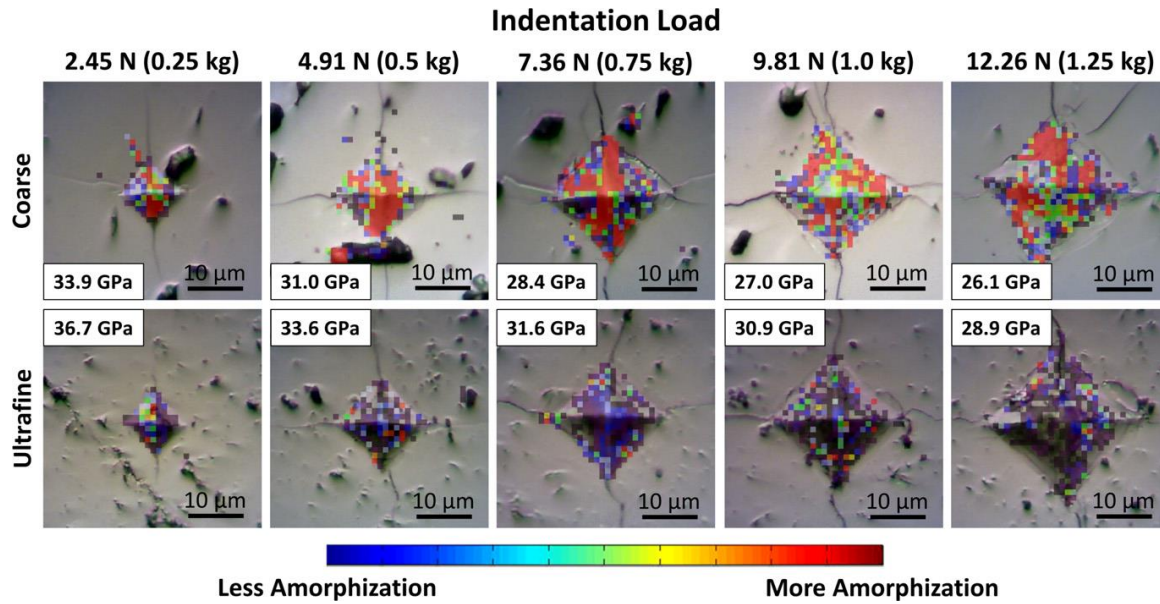


Fig. 2. Spatial distribution of amorphization intensity in coarse- and ultrafine-grained B₄C at various loads. Static hardness values at each load are also indicated.

3. TEM analysis of deformed B_4C regions revealed that amorphized regions contain dislocations and amorphization causes lattice distortion leading to residual stresses and initiation of micro cracks. These results are shown in Fig. 3 and published in an Editor Invited Viewpoint Article, “In Search of Amorphization-Resistant Boron Carbide” G. Subhash, A.P. Awasthi, C. Kunka, P. Jannotti and M. DeVries, *Scripta Materialia* (2016) 158-162.

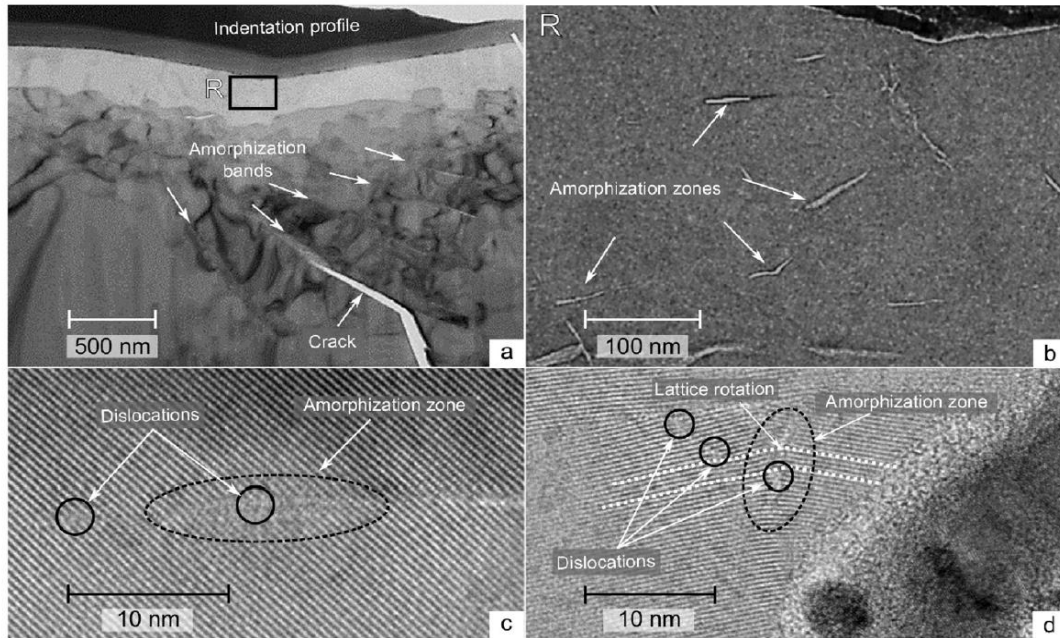


Fig. 3. (a) TEM revealing amorphization bands and a crack beneath indentation on a boron carbide sample. (b) Magnified region (R) showing dispersed amorphization zones. (c) and (d) are higher magnifications in the vicinity of amorphization zones and show lattice-level details, including dislocations and lattice rotation. Lattice dislocations are indicated by solid circles.

4. 3D maps of residual stress were generated for static and dynamic Vickers indentations based on the concurrent shift of the 1088 cm^{-1} peak in the Raman spectra, as shown in Fig. 4. Residual stress appears to be higher near the intact amorphized regions and lower near cracks due to stress relaxation and graphitic inclusions which buffer the stress. The results also suggest that the process of amorphization causes a volumetric expansion of the affected material relative to its formerly pristine crystalline state. This expansion causes compressive residual stress in the surrounding crystalline matrix which may be responsible for the observed amorphous peak in the Raman Spectrum. In addition, dislocations and lattice rotation surrounding the amorphized islands were also argued to impart residual stresses in the material. The manuscript containing these results, titled “Amorphization-Induced volume change and residual stresses in Boron Carbide”, has been submitted to *Journal of the American Ceramic Society* and is awaiting peer review.

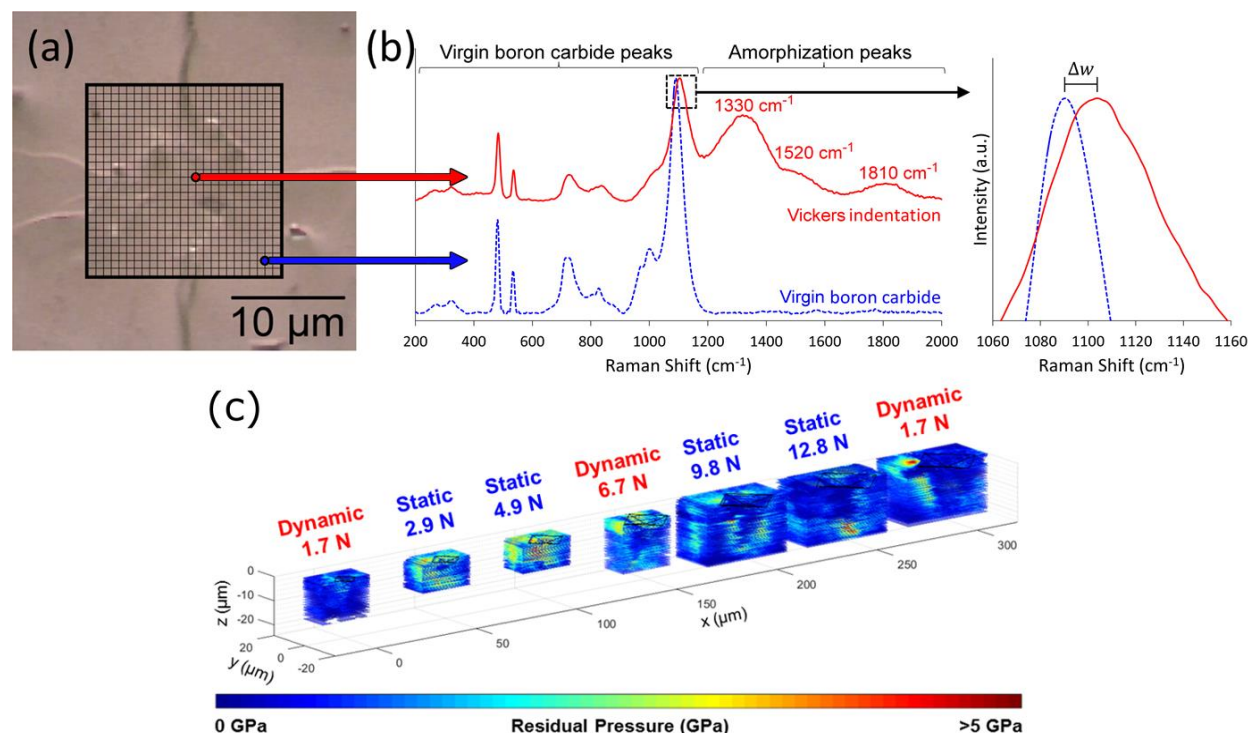


Fig. 4. (a) An exposed region beneath a Vickers indentation is scanned with Raman spectroscopy at various points to collect (b) Raman spectra, which can be used to generate two-dimensional maps of amorphization based on stress-induced shifting of the most prominent peak of virgin boron carbide (Δw). Such maps are compiled into (c) three-dimensional representations of residual stress beneath each Vickers indentation.

5. Using DFT, the theoretical Raman spectra for more than 50 polymorphs were evaluated and a procedure for identifying the polymorphs formed in a fabricated boron carbide sample was developed. The procedure has been shown to be applicable on hot pressed (HP) and spark plasma sintered (SPS) boron carbide (see Fig. 5) specimens. These results are published in two papers: (i) C. Kunka, A. Awasthi, G. Subhash, "Evaluating boron-carbide constituents with simulated Raman spectra" *Scripta Materialia*, 138 (2017) 32-34; and (ii) C. Kunka, A.P. Awasthi, and G. Subhash, "Crystallographic and spectral equivalence of boron-carbide polymorphs," *Scripta Materialia*, 122 (2016) 82-85

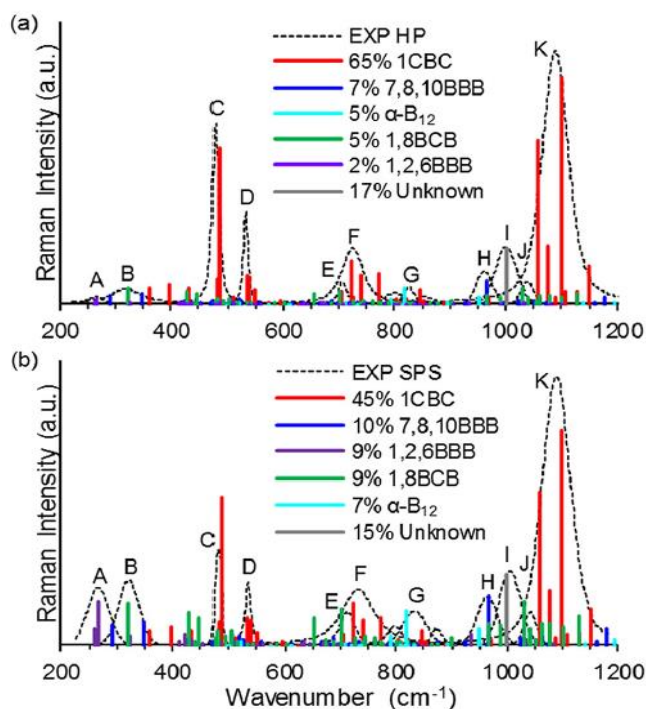


Fig. 5. Fitting of deconvoluted experimental Raman spectra (dotted curves) with DFT simulations to identify relative abundances of polymorphs in boron carbide. Differences between (a) HP and (b) SPS processed boron carbide seem to be merely relative abundances of polymorphs.

6. The DFT study also identified large cage spaces in the boron carbide crystal structure which have been postulated to be responsible for its low density as well as its propensity for amorphization. The cage space is large enough to accommodate large atoms which can potentially mitigate the propensity for amorphization by providing bending resistance for the chain atoms of the unit cell. Based on the size of the cage space and atomic radii of elements, a large number of atoms are identified as potential dopants for boron carbide. Fig. 6 illustrates the cage space and atoms of elements that are of size capable of occupying the cage space. These results are published in an Editor Invited Viewpoint Article: “In Search of Amorphization-Resistant Boron Carbide” G. Subhash, A.P. Awasthi, C. Kunka, P. Jannotti and M. DeVries, *Scripta Materialia* (2016) 158-162.

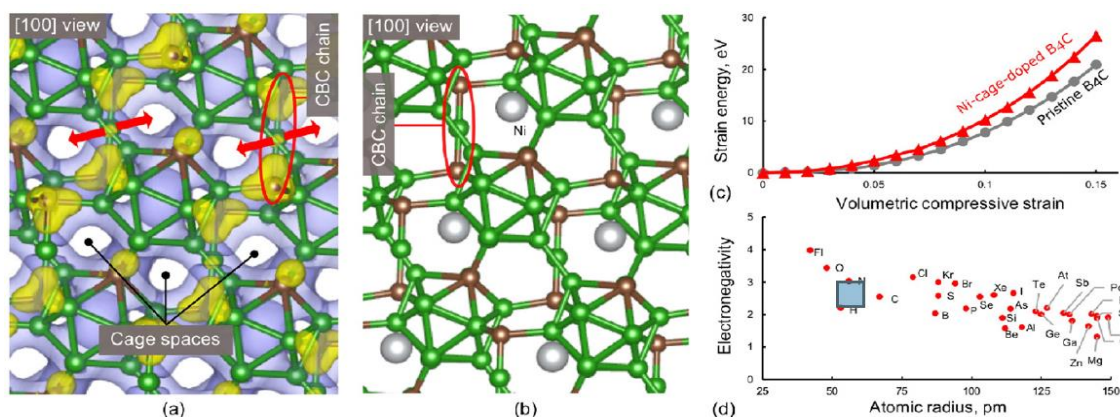


Fig. 6. (a) Isosurfaces (3-D contour maps) representing high (yellow) and low (blue) levels of spatial distribution of electron density in boron-carbide crystal structure. White areas represent regions with electronic density below 20% of the maximum value and are termed “cage spaces.” Red arrows depict how the chains are susceptible to bending/buckling into cage-spaces. These spaces are continuous, and their sizes are sufficient to accommodate additive atoms. Green atoms are boron while brown are carbon. (b) Ni-cage-doped B₄C used for DFT modeling. (c) DFT results of relative performance in volumetric compression for pristine and Ni-cage-doped B₄C. (d) Electronegativity versus atomic radius of single atoms of different elements of the periodic table.

7. Further DFT-simulations were performed to seek the dependence of the α -boron (α -B₁₂), (B₁₂)CCC and graphite constituents on the Raman spectra at different levels of hydrostatic pressure ranging from 0-150 GPa. It was found that these constituents must be stressed in the range of 60-110 GPa to occupy the amorphous spectral locations (Fig 7). This suggests that the region around the amorphous zone must be locked in a high stress state even after unloading, leading to a new understanding of the immediate region surrounding the amorphous zone, which can be broken down into 4 components as shown in Fig 8. The first region (Region 1 in Fig 8) consists of completely amorphized material which perhaps does not have any Raman spectrum. This region is also very tiny and hence its contribution to the overall Raman is miniscule. Region 2 contains α -boron (α -B₁₂), (B₁₂)CCC and graphite under high pressures (in the range 90-110 GPa). Our calculations show that even the most abundant polymorph of boron carbide, namely (B₁₁C_p)CBC is a likely constituent of this region, as its stressed Raman spectrum also falls in the experimental amorphized band. (The high intensity low frequency peak is due to a transition state which would be seen experimentally.) The third region (Region 3 in Figure 8) is a region of low stresses in the range 0-10 GPa which would cause crystalline peaks to shift and the surrounding material (Region 4) is essentially stress free and would hence emanate crystalline spectra. The combined spectrum is a superposition of spectra emanating from all regions. This work is being submitted to *Progress in Materials Science*.

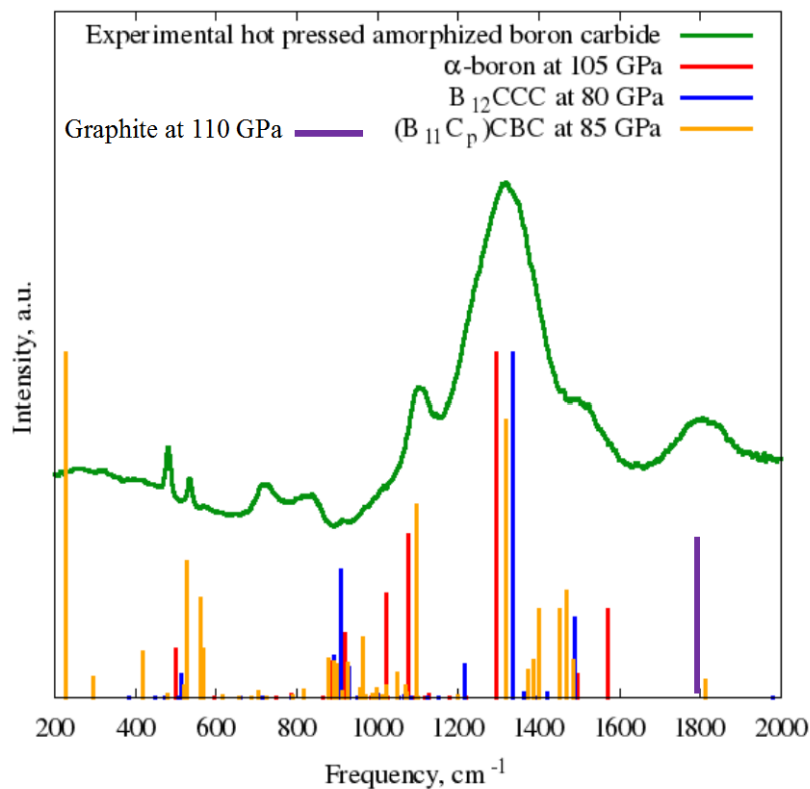


Fig 7. Spectral locations of stressed constituents, reverse engineered to fit experimental amorphous bands in boron carbide.

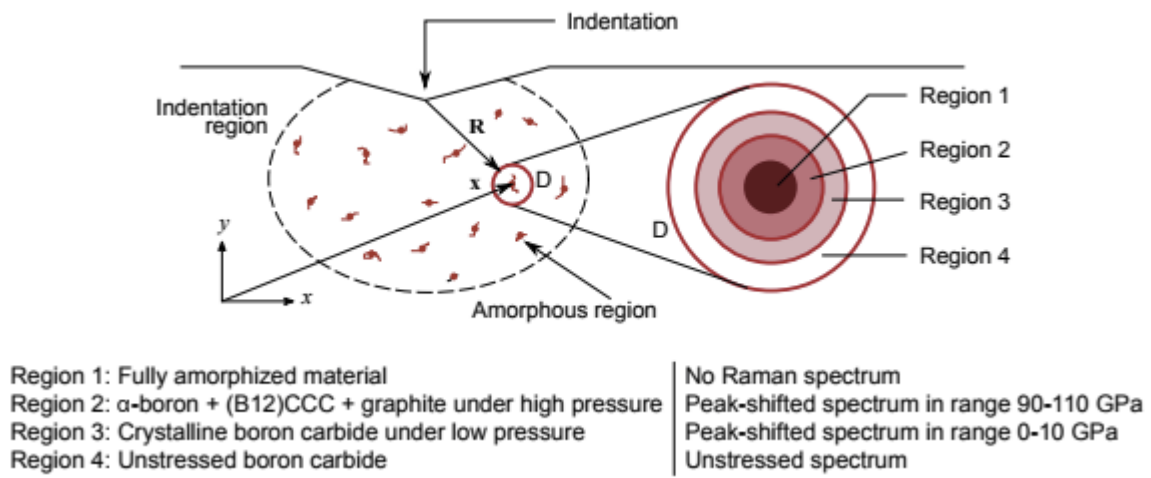


Fig 8: Idealization of neighborhood around the amorphized zone for simplifying the breakdown of cumulative Raman spectra.

8. An extended Mohr-Coulomb model was developed to capture the normalized pressure-dependent shear strength of a variety of brittle materials over a wide range of pressures. This model is not only able to capture the linear response of brittle ceramics at low pressures, but also the experimentally observed nonlinear response at higher pressures up to HEL and the pressure-independent response beyond HEL with a single curve, as shown in Fig. 9. Further, the constants used in this model are shown to be universal and applicable to most brittle materials. This feature greatly reduces the requirement on experimental data, since knowledge of a material's HEL is the only requirement in the extended Mohr-Coulomb model. This is a major advantage in modelling the behavior of new materials, where relevant experimental data may not be available to determine each materials' constants for use in other models such as Mohr-Coulomb, Drucker-Prager and JH-2. The details of this model have been published in M. Shafiq and G. Subhash "An Extended Mohr-Coulomb Model for Fracture Strength of Intact Brittle Materials under Ultrahigh Pressures", *Journal of the American Ceramic Society* 99 (2016) 627-630. A manuscript comparing this new model to other established models in literature has been submitted to *Journal of the American Ceramic Society* and is awaiting peer review.

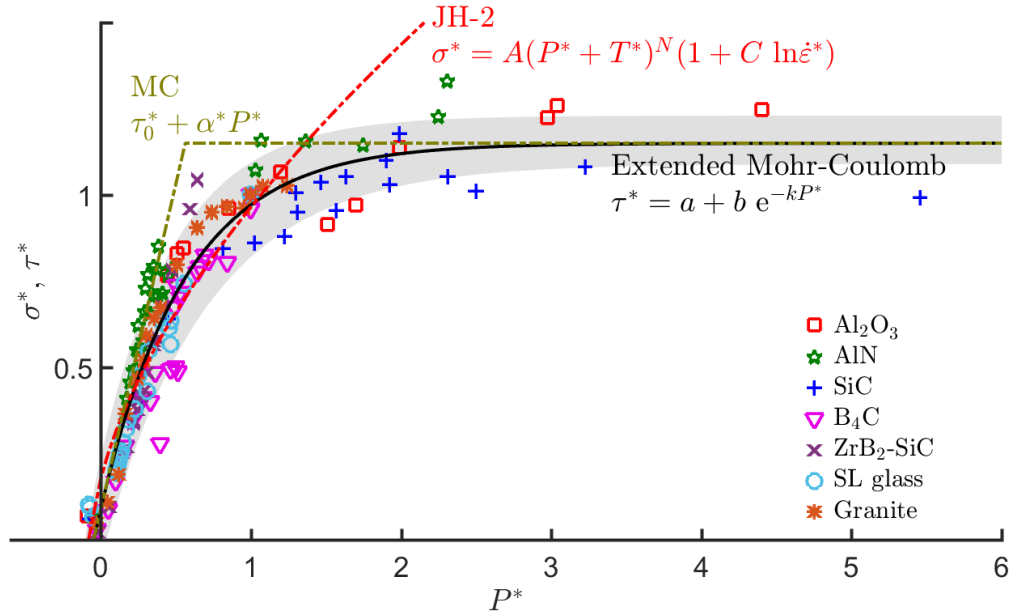


Fig. 9. Experimental data for intact ceramics normalized by the corresponding P_{HEL} and τ_{HEL} values along with the Mohr-Coulomb (MC), JH-2 and extended Mohr-Coulomb models. The bilinear Mohr-Coulomb (MC) model is unable to capture the inelastic response at higher pressures while the JH-2 model fails to capture the pressure independent strength saturation beyond HEL. The 99% confidence interval for the extended Mohr-Coulomb model is represented by the grey band.

9. Utilizing the extended Mohr-Coulomb model, an improved dynamic expanding cavity model (d-ECM) was developed, which more accurately captures the experimentally observed target resistance of structural ceramics, as shown in Fig. 10. This model is less computationally demanding than the conventional dynamic expanding cavity model. It was found that, similar to the case of intact ceramics, the pressure-shear response of multiple comminuted ceramics can be predicted from a single set of universal constants in the new d-ECM, thus allowing the model to be used to estimate a material's ballistic capability without the need for additional experimental data. A sensitivity analysis using the d-ECM revealed that the properties of the comminuted ceramic, particularly its dynamic shear strength, has a greater influence on the target resistance of ceramics than those of the corresponding intact material. These results are published in "An Improved Dynamic Expanding Cavity Model for High-Pressure and High-Strain Rate Response of Ceramics" S. Bavdekar, G. Parsard, G. Subhash, and S. Satapathy, *International Journal of Solids and Structures*, (2017) 77-88.

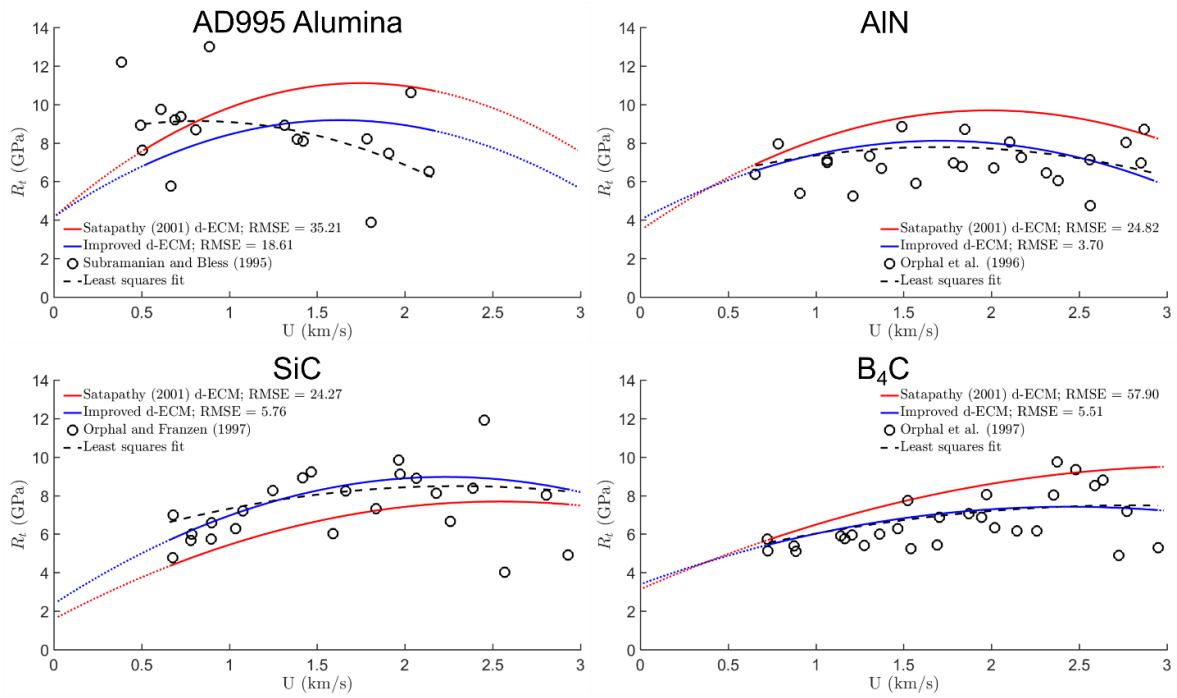


Fig. 10. Comparison of the predictive capability of improved d-ECM model with that of the conventional model (Satapathy, 2001) on various structural ceramics.

Publications:

- Amnaya Awasthi (PG)⁺, Ghatu Subhash*, "Deformation behavior and amorphization in icosahedral boron-rich ceramics", *Progress in Materials Science* (submitted)
- S. Bavdekar⁺ and G. Subhash*, "Comparison of Pressure-Sensitive Strength Models for Ceramics Under Ultrahigh Confinement", *Journal of the American Ceramic Society* (submitted)
- G. Parsard⁺ and G. Subhash, "Amorphization-Induced volume change and residual stresses in Boron Carbide", *Journal of the American Ceramic Society* (submitted)
- C. Kunka⁺, A.P. Awasthi (PG)⁺, and G. Subhash*, "Evaluating Boron-Carbide Constituents with Simulated Raman Spectra" *Scripta Materialia* 138 (2017) 32-34; <http://dx.doi.org/10.1016/j.scriptamat.2017.05.030>
- G. Parsard⁺ and G. Subhash*, "Raman Spectroscopy Mapping of Amorphized Zones Beneath Static and Dynamic Vickers Indentations on Boron Carbide," *Journal of the European Ceramic Society* 37 (2017) 1945-1953; <http://dx.doi.org/10.1016/j.jeurceramsoc.2016.12.045>
- S. Bavdekar⁺, G. Parsard⁺, G. Subhash*, and S. Satapathy "An Improved Dynamic Expanding Cavity Model for High-Pressure and High-Strain Rate Response of Ceramics" *International Journal of Solids and Structures* 125 (2017) 77-88 <https://doi.org/10.1016/j.ijsolstr.2017.07.014>
- G. Subhash*, A.P. Awasthi (PG), C. Kunka⁺, P. Jannotti⁺ and M. DeVries⁺, "In Search of Amorphization-Resistant Boron Carbide" Editor Invited 'Viewpoint Article' in *Scripta Materialia* (2016) 158-162; doi:10.1016/j.scriptamat.2016.06.012
- M. Shafiq⁺ and G. Subhash* "An Extended Mohr-Coulomb Model for Fracture Strength of Intact Brittle Materials under Ultrahigh Pressures", *Journal of the American Ceramic Society* 99 (2016) 627-630. DOI: 10.1111/jace.14026
- C. Kunka (G), A.P. Awasthi (PG), and G. Subhash*, "Boron-carbide polymorphs: nomenclature, equivalence and Raman spectra", *Scripta Materialia*, 122 (2016) 82-85 doi:10.1016/j.scriptamat.2016.05.010